A SCHEME OF QUALITATIVE ANALYSIS INVOLVING THE USE OF ORGANIC REAGENTS

A THESIS

Submitted in partial fulfillment
of the requirements for the Degree
of Master of Science in Chemistry

by

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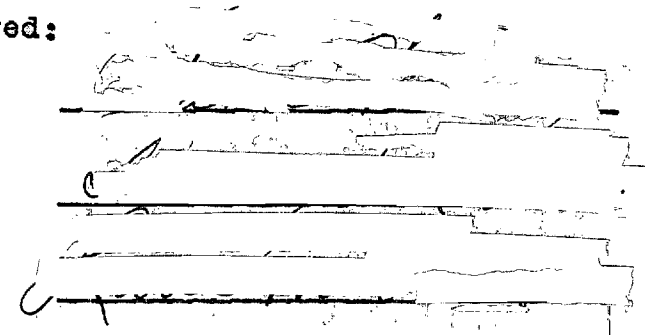
Atlanta, Georgia
1940

The author wishes to express his sincere appreciation to Dr. H. L. Edwards both for suggesting this problem and for his helpful assistance throughout the course of the investigation.

Approved:



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1. INTRODUCTION

The classic method for the separation and identification of the metallic ions was developed by A. A. Noyes of the Massachusetts Institute of Technology. This scheme employs gaseous hydrogen sulfide as its chief group precipitant. While various modifications of Noyes' system have been suggested, they all make use of hydrogen sulfide for group separations. Unfortunately, the use of this gas has several distinct disadvantages: (1) its vapors are relatively poisonous; (2) it has an objectionable odor; (3) it is somewhat difficult to generate; and, (4) because of its nature, it is very inefficient as a precipating reagent.

In order to obviate these and other difficulties attendant upon the use of hydrogen sulfide gas, numerous schemes have been devised. Among the outstanding methods that have been suggested are those devised by Almkvist and by Vortman. N. Alvanez has proposed the use of thioacetic acid, which, while precipitating the metals as the sulfides, eliminates many of the disadvantages of gaseous hydrogen sulfide.

C. J. Brockman of the University of Georgia has developed a method of analysis of the metals without the use of hydrogen sulfide, which is worthy of note. His scheme divides the metals into six groups, the first of

which is essentially the same as the Silver group in the hydrogen sulfide scheme of analysis. The second group consists of the sulphates insoluble in water. The third is the amphoteric group, while the fourth consists of the metals which, with excess ammonia, form insoluble phosphates. Group five contains the metals which form soluble ammonia complexes, and group six comprises the alkalies.

The field of organic chemistry has been investigated by many Analytical Chemists in the belief that in it might be found compounds which will serve both as group precipitants and as final confirmatory reagents. The work of R. Berg, who studied the reactions of 8-hydroxyquinoline with the metallic ions, of Baudisch and King, who have shown the value of cupferron, the ammonium salt of nitrosophenylhydroxylamine, as a reagent for iron and copper, and of many others, proves the value of organic compounds in analytical chemistry.

H. L. Edwards, working with J. T. Dobbins and E. C. Markham of the University of North Carolina, has developed a scheme utilizing organic reagents which is worthy of consideration. His method employs a pyridine-thiocyanate reagent to precipitate the heavy metals, and ammonium carbonate to precipitate the alkaline earths. The Silver group is unchanged. From these groupings, organic reagents are used for the identification of the individual metallic ions.

In the course of the present study, many organic compounds have been investigated with the purpose of

determining their value as analytical reagents. A few of these possess the unique property of reacting with only one or perhaps two metallic ions under certain conditions, and may thus be utilized as "spot tests".

A scheme of analysis involving the use of these organic reagents has been devised, and, in view of the rapid method of analysis which they afford and the ease with which they may be employed, it is felt that this method will have many advantages over the older, classical scheme. The procedure has been so designed that the reagents may be utilized in a semi-micro method of analysis, but they will serve equally as well in the ordinary methods of macro-analysis.

11. THEORETICAL CONSIDERATIONS

In 1892 Alfred Werner suggested a theory of valency, in an attempt to explain the structure of a series of so-called " molecular " or " complex" compounds formed by the combination of apparently saturated molecules. According to Werner's theory, molecular structure was to a great extent determined by the tendency of certain atoms to attach to themselves a definite number, called the co-ordination number, of other atoms or groups, or even whole molecules, capable of independent existence. Every atom had a maximum co-ordination number, usually, although not always, four or six.

This conception of the co-ordination number is of fundamental importance in Werner's theory. However, another important fact is apparent from a study of the formulas of certain of these compounds: it is possible for a singly charged anion to replace a neutral molecule within a co-ordinate group. The development of the electronic theory has aided in interpreting Werner's ideas of molecular structure. It is clear, first of all, that the linkages which join the units of the co-ordination complex to the central atom are covalent, rather than polar. In the former type of linkage, the electrons are shared jointly by the groups involved, while in the latter, an electron is actually transferred from one atom to another. The attachment of a univalent radical, such as chlorine, is a coval-

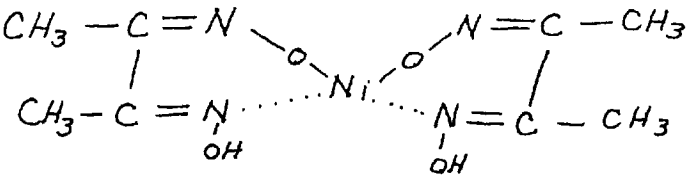
ency of the normal type, in which each of the atoms involved contributes one electron. An independent molecule, such as ammonia, on the other hand, which already has an even number of valency electrons and hence cannot form a union of this type, must be attached to the central atom by a co-ordinate link, that is, the nitrogen atom furnishes both of the necessary electrons. Any molecule capable of entering into a complex in this way must have one lone pair of electrons. The number of shared electrons in the valency group of the central atom, thus, is the same whether the co-ordinate groups are molecules or univalent radicals, and it is consequently possible for those of one kind to replace those of the other, within the complex.

Werner's theory has been found applicable to the whole of chemistry, organic as well as inorganic. The same electronic principles can be applied to both, although only inorganic compounds have been considered so far.

Many molecules enter the co-ordinated group forming the metallo-organic compounds. The metallic complexes of thiourea and ethylenediamine are examples of this type. The formation of the co-ordinate bond with the central atom is made possible through the unshared electron pair of nitrogen, which most of these compounds contain. The presence of nitrogen is not a prerequisite, however, for other atoms in the molecule may possess the electron pair.

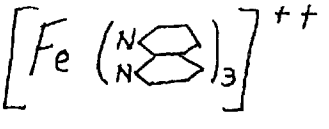
Ring structures frequently occur with these compounds. When an organic molecule has two points of attach-

ment to the central atom through the co-ordinate groups, the substance is known as an inner complex or chelate compound. Nickel-dimethylglyoxime is an excellent example, for it has a primary valence of two and a co-ordination number of four.



Each organic molecule is attached to nickel at two points; forming a chelate compound consisting of two six-membered rings. Nickel has taken the place of a hydrogen atom in each of the two organic molecules, forming covalent bonds with the oxygen atoms originally attached to the hydrogen atoms, while the unshared pair of electrons originally on the nitrogen atoms of the other two (-N-OH) groups now form two co-ordinate covalent bonds with the nickel. Other compounds of the same general formula may react just as does dimethylglyoxime.

Characteristically colored compounds are produced by the reaction between neutral organic compounds and metals. Secondary valence forces alone are sufficient to form addition compounds with some inorganic compounds. a,a'-dipyridyl is an example of this.



Still another type of complex formation is that of adsorption complexes; that is, combinations of organic components by auxiliary valences in non-stoichiometric ratios.

The absorption of quinalizarin by magnesium hydroxide is probably an example of this type.

111. THE PRESENT SCHEME

It has been found advisable in the present, as in the older schemes of analysis, to effect the separation of the metallic ions into a number of smaller groups. After such separation, which has been accomplished without the use of the objectionable hydrogen sulfide gas, organic reagents have been found which are sufficiently specific in their action to make possible the identification of the metals with a minimum of further separation.

In this scheme, the analysis of the Silver or Hydrochloric acid group has not been changed, for it has stood the test of time and has proved itself to be the simplest and most rapid method for the identification of these ions.

In the further separation of the metals into groups, advantage is taken of the fact that the heavy metals form insoluble hydroxides upon the addition of ammonia solution and at the same time the ammonium complexes of copper, cadmium, nickel, cobalt, and zinc are formed. This affords a separation of these metals. The alkalies and alkaline earths are, of course, uneffected by this treatment, and, by the addition of ammonium carbonate, the alkaline earths, barium, strontium, and calcium, are precipitated and separated from the alkalies, sodium, potassium, and ammonium.

Advantage is also taken of the amphoteric nature of aluminum, antimony, chromium, and tin, for they are dissolved in sodium hydroxide, and thus furnish another separation.

Since chromates interfere, they are removed by the addition of hydrogen peroxide, which reduces the chromate to the chromic form. This treatment will also reduce permanganates to the manganic state.

Arsenates and phosphates will also interfere by precipitating barium, strontium, and calcium along with the insoluble hydroxides. Hence, their presence must be determined before the solution is made basic. This is ascertained by means of the ammonium molybdate test. Individual portions of the precipitate are tested for the presence of arsenates or phosphates.

Rather than attempt to remove these ions, an alternate scheme has been devised in which their presence will not interfere. In this alternate scheme, group lll-B is combined with group ll-B, as shown in chart ll. When the solution is made basic with ammonia, the phosphates of barium, strontium, and calcium will precipitate with the insoluble hydroxides of group ll-B. They are uneffected by the sodium hydroxide treatment. By acidifying the residue, and adding a sulfate, the alkaline earth metals can be removed. After conversion to the carbonates, they are identified according to the original scheme. These ions will not interfere with the tests of Group ll-B, but the phosphates and arsenates do interfere with the test for Mg by precipitating it as magnesium phosphate or arsenate, along with iron. Hence sodium tartrate is added to the neutral solution in order to remove

the interferences of iron, and magnesium is detected with diphenylcarbarzide. The remaining groups are analysed in the usual manner.

While in many cases, it is not possible to give formulas for the metallo-organic compounds which are formed, other examples will be cited where the formulas have been definitely worked out. In general, the organic compound is attached to the metal either by electrovalent or co-ordinate valences or possible combinations of these. Some compounds are merely oxidized by the metal and thus undergo internal rearrangements. Others are held by co-ordinate valences and require the addition of a negative group or ion for precipitation, such as the quinoline-iodide precipitates.

It has been noted throughout this investigation that the sensitivities of the tests are greatly increased by carrying out the reactions on filter paper. This is perhaps due to capillary phenomena which spread the solution out and thus in some manner render the tests more sensitive. This method of testing has been utilized wherever possible. Spot plate reactions have also been found very satisfactory and are frequently used.

By using semi-micro equipment a great saving is effected in materials. A few of the organic reagents are relatively expensive at the present time, and so by carrying out the reactions on a semi-micro scale, an additional advantage is obtained.

Through the use of spot tests, the time ordinarily lost through precipitation and filtration is saved. These tests eliminate the necessity for further separations once the original groups are isolated. The advantage which such a method offers is quite obvious in that the rapidity of the analysis is greatly increased.

In this investigation, the properties of thirty-five organic compounds have been studied from an analytical standpoint, and relatively inexpensive ones, which best suit the conditions of the experiment, have been chosen.

Wherever the use of aminopyrine is mentioned, brucine sulfate, acridine, methylbenzothioazole, and quinoline may be substituted, for all these alkaloids give similar reactions in the presence of potassium iodide. Aminopyrine is used mainly because it is the least expensive and can be conveniently purchased at any drug store in pure form.

CHART 1.

GENERAL SCHEME

Solution contains all the metals in the form of salts. Acidify with HNO_3. Add two cc. of H_2O_2 to reduce chromate and permanganate. Then add sufficient 3N HCl to complete the precipitation and filter.

Ppts. Group 1

$AgCl$
$PbCl_2$
$HgCl$

To a 1 cc. portion add ammonium molybdate soln.

Yellow ppt. indicates PO_4 or AsO_4.

If either is present proceed according to Scheme 11, Chart 11.

Filtrate: Contains Groups 11-1V. Add conc. nitric acid and heat to oxidize As''', Fe'', and Sn''.

To remainder of solution, add conc. ammonium hydroxide until neutral and then 10 cc. in excess.

Ppts. Gr. 11 Hydroxides of Bi''', Mg'', Sn'''', Mn'', Fe''', Cr''', and Al'''. $HgNH_2Cl$, Sb_2O_3

Add NaOH soln.

Ppt. Gr.11-B Hydroxides of Bi''', Mg'', Mn'', and Fe''', $HgNH_2Cl$ and Sb_2O_3

Filt. Gr.11-A Soln. of $SnO_3^=$, SbO_4^-, CrO_2^-, and AlO_2^-

Filtrate: Contains Groups 111-V. Add ammonium carbonate.

Ppts. Gr.111-B Carbonates of Ba'', Ca'', and Sr''.

Filtrate: Contains Groups 111-A and 1V. Make neutral with HNO_3. Add ammonium carbonate.

Ppts. Gr.111-A Carbonates of Cu'', Cd'' Ni'', Co'', and Zn''

Filt. Gr.1V Na', K', and NH_4'

CHART 11.

GENERAL SCHEME IN PRESENCE OF

PHOSPHATES OR ARSENATES

Solution contains all the metals in the form of salts.
Acidify with nitric acid and add hydrogen peroxide to reduce chromate and permanganate.
Add dilute (3N) HCl and filter.

Ppts.

Group 1

$AgCl$
$HgCl$
and
$PbCl_2$

Filtrate

Test a portion for AsO_4 and PO_4^{---} as in Chart 1

Add conc. HNO_3 to oxidize As''',Fe'', and Sn''.

To remainder of solution add conc. NH_4OH until neutral and then 10 cc. in excess.

Filtrate

Contains Groups 111-A and 1V.

Ppts. of hydroxides of Bi''', Mg'',Mn'',Fe''',Cr''',Al''', and Sn'''', and $HgNH_2Cl$ and Sb_2O_3, and phosphates of Ba'', Ca'', and Sr''.

Add 20 cc. of 6N NaOH and warm.

Filt.

Grs. 11-A

Ppts. of hydroxides of Bi''',Mg'',Mn'',Fe''', and $HgNH_2Cl$, and Phosphates of Ba'',Sr'' and Ca''.

Acidify with HCl. Add ammonium sulfate soln.

Filt.

Gr.111-B Soln. of Bi''', Hg'', Mg'', Mn'', and Fe'''.

Ppts. Sulfates of Ba'', Ca'', and Sr''. Boil in soln. of ammonium carbonate. Filter.

Filt.

Discard.

Ppts.

Carbonates of Ba'', Ca'', & Sr''. Gr.111-B.

1V. LABORATORY PROCEDURE

PREPARATION OF THE SOLUTION FOR ANALYSIS.

Section 1. A quantity of the material is taken for analysis so that approximately 50 mg. of each metal ion will be present. If the substance is water soluble, it is dissolved in 20 cc. of water; if water-insoluble, it is dissolved in the appropriate acid, the solution evaporated almost to dryness, and the residue redissolved in 20 cc. of water, to which a small amount of acid is added, if necessary.

If the color of the original solution indicates the presence of either the chromate or permanganate ion, it will be necessary to reduce it to the chromic or manganous condition, so that insoluble salts will not be formed when the solution is made basic for the group separations. This is accomplished by treating the above solution with 2 cc. of 3% hydrogen peroxide and boiling for 3-4 minutes. If the solution is colorless, the absence of both chromate and permanganate ions is indicated, and the hydrogen peroxide treatment may be omitted.

Section 2. PRECIPITATION AND ANALYSIS OF GROUP 1.

The precipitation of the group 1 metals is accomplished by adding chloride ions, in the form of dilute hydrochloric acid, to the prepared solution. The insoluble *chlorides of silver, lead, and mercurous mercury constitute* Group 1. The filtrate, containing the ions of Groups 11-1V, is set aside for treatment according to Section 3. The

CHART 11.

GENERAL SCHEME IN PRESENCE OF

PHOSPHATES OR ARSENATES

Solution contains all the metals in the form of salts.
Acidify with nitric acid and add hydrogen peroxide to reduce chromate and permanganate.
Add dilute (3N) HCl and filter.

Ppts.

Group 1

$AgCl$
$HgCl$
and
$PbCl_2$

Filtrate

Test a portion for AsO_4 and PO_4 as in Chart 1

Add conc. HNO_3 to oxidize As''', Fe'', and Sn''.

To remainder of solution add conc. NH_4OH until neutral and then 10 cc. in excess.

Filtrate

Contains Groups III-A and IV.

Ppts. of hydroxides of Bi''', Mg'', Mn'', Fe''', Cr''', Al''', and Sn'''', and $HgNH_2Cl$ and Sb_2O_3, and phosphates of Ba'', Ca'', and Sr''.

Add 20 cc. of 6N NaOH and warm.

Filt.

Grs. II-A

Ppts. of hydroxides of Bi''', Mg'', Mn'', Fe''', and $HgNH_2Cl$, and Phosphates of Ba'', Sr'' and Ca''.

Acidify with HCl. Add ammonium sulfate soln.

Filt.

Gr. III-B Soln. of Bi''', Hg'', Mg'', Mn'', and Fe'''.

Ppts. Sulfates of Ba'', Ca'', and Sr''. Boil in soln. of ammonium carbonate. Filter.

Filt.

Discard.

Ppts.

Carbonates of Ba'', Ca'', & Sr''. Gr. III-B.

CHART 111.

ANALYSIS OF GROUP 1

Residue from the treatment with HCl may be $PbCl_2$, AgCl, or HgCl.
Wash on filter paper with 3 cc. of dilute HCl and discard washings. Pour over the precipitate 5 cc. of hot water and collect in test tube.

Filtrate may contain Pb''. Add HOAc and K_2CrO_4 soln. Yellow ppt. shows presence of Pb''.

Ppt. may be AgCl, HgCl, and some undissolved $PbCl_2$. Wash with hot water until all $PbCl_2$ has been dissolved as shown by testing wash water with sulfuric acid. Pour 10 cc. of dilute ammonia soln. on the residue in the filter paper and catch filtrate in a small beaker.

Filtrate may contain $Ag(NH_3)_2^+$. Add dilute HNO_3 until solution becomes acid. Formation of white ppt. indicates presence of Silver.

Residue may consist of a black mixture of Hg and $HgNH_2Cl$. Dissolve in aqua regia, boil to decompose excess aqua regia, dilute with water, filter if necessary, and add to clear soln. a few drops of $SnCl_2$. A white ppt. turning gray or black, indicates the presence of Hg.

residue, after filtering, is washed with 5 cc. of dilute HCl. Five cc. of hot water are then poured repeatedly over the precipitate. The filtrate thus produced may contain lead. To this filtrate is added 1 cc. of acetic acid and one cc. of potassium chromate. A yellow precipitate indicates the presence of lead.

If the residue contains lead, it is washed with hot water until the filtrate no longer gives a precipitate with dilute sulfuric acid. Then 10 cc. of dilute ammonia solution are poured over the residue, and the filtrate caught in a small beaker or test tube. Nitric acid is added until the solution becomes acid. The formation of a white precipitate or turbidity indicates the presence of silver.

The residue remaining on the filter paper may consist of a black mixture of Hg and $HgNH_2Cl$. This residue is transferred to a small evaporating dish, 2 cc. of aqua regia are added to dissolve the precipitate, and the solution is evaporated to a few drops in order to destroy the excess aqua regia. Two cc. of water are added, the mixture is filtered if necessary, and the clear solution treated with a few drops of stannous chloride. A white precipitate turning gray or black, confirms the presence of Hg.

Section 3. DETECTION OF ARSENATES AND PHOSPHATES.

To the filtrate, after the removal of Group 1, are added 5 cc. of concentrated nitric acid and the mixture heated to boiling in order to effect the oxidation of As'''', Fe'', and Sn''. Two cc. of the resulting solution are made

acid by the addition of two cc. of concentrated nitric acid. This is heated to boiling and two cc. of ammonium molybdate solution are added. The solution is allowed to stand for five minutes. The formation of a yellow precipitate indicates the presence of phosphate or arsenate. The precipitate is separated by centrifuging and is dissolved in dilute ammonia. The solution is divided into two portions. One portion is acidified with 3N sulfuric acid. Two cc. of hydroquinone reagent are added, and the solution is allowed to stand for one minute. The appearance of a blue color in the solution shows the presence of phosphate ions(1).

The other portion is allowed to flow slowly into a slightly acid solution of silver nitrate. The formation of a chocolate brown precipitate proves the presence of arsenate ions.

If either phosphates or arsenates are found to be present, Scheme 11 must be followed; if they are absent, Scheme 1 should be used.

The hydroquinone reagent will detect phosphates in the presence of arsenates, and will not react with arsenates unless allowed to stand for two minutes or more.

Section 4. PRECIPITATION OF GROUP 11.

The remainder of the solution after the removal of Group 1 is made basic with concentrated ammonia and then 5 cc. in excess are added. The insoluble hydroxides of Bi^{+++}, Sn^{++++}, Mn^{++}, Fe^{+++}, Cr^{+++}, Al^{+++}, and Mg^{++} and $HgNH_2Cl$ and Sb_2O_3. are thus precipitated, while the soluble ammonia complexes of Cu^{++},Cd^{++},Ni^{++},Co^{++}, and Zn^{++} are formed. This residue is designated as Group 11 and the filtrate as Group 111.

The residue is treated with 20 cc. of 6N NaOH in order to dissolve out the amphoteric elements; Cr^{+++}, Al^{+++},Sb^{+++}, and Sn^{++++}. The remaining insoluble hydroxides of Bi^{+++},Mn^{++},Fe^{+++}, and Mg^{++} and $HgNH_2Cl$ are designated as Group 11-B and the soluble complexes of Al^{+++},Cr^{+++},Sb^{+++}, and Sn^{++++} as Group 11-A.

Section 5. IDENTIFICATION OF MEMBERS OF GROUP 11-B.

The residue consisting of the insoluble hydroxides of Bi^{+++},Mn^{++},Fe^{+++}, and Mg^{++} and $HgNH_2Cl$ is dissolved in 3N HCl and two cc. in excess are added. The solution is divided into five equal parts in order that two tests may be made for each ion present.

(1) To one cc. of the first portion, two drops of KCNS solution are added. A blood-red solution of ferric thiocyanate indicates the presence of iron.

To one cc. of the solution three drops of amino-pyrine reagent are added. The formation of a purple color in the solution indicates the presence of iron.

Chart IV.

ANALYSIS OF GROUP II-B

Add dilute HCl until hydroxides of Bi,Mg,Fe, and Mn and $HgNH_2Cl$ dissolve. Divide solution into five equal parts.	
1.	To one portion, add KCNS. A blood-red solution indicates the presence of Fe'''. To another one cc. portion, add three drops of aminopyrine solution. A purple color indicates the presence of iron.
2.	To one cc. of solution, three drops of thiourea solution is added, which imparts a light yellow color to the solution if Bi''' is present. To another one cc. portion, three drops of 1-methylbenzothiazole are added, followed by three drops of Kl solution. The formation of an intensely red precipitate, proves the presence of Bi'''.
3.	To a one cc. portion, made basic with ammonia, are added three drops of benzidine solution. A deep blue color proves the presence of Mn''.
4.	A one-half cc. portion is poured on filter paper. To this is added $SnCl_2$ solution, followed by *three drops of aniline*. *The appearance of finely* divided black specks, proves the presence of Hg''.
5.	To a one cc. portion of test solution is added one cc. of 50% solution of ammonium nitrate and an excess of 3N ammonium hydroxide is then added. The mixture is then filtered. To the filtrate, is added four drops of oxine. A heavy yellow precipitate proves the presence of Mg''. Another portion of the filtrate is treated with NaOH until alkaline, and two drops of quinalizarine are added. The formation of a cornflower-blue absorption lake shows the presence of Mg''.

This is assumed to be due to a dye of complex composition.

(2) In order to test for Bismuth, three drops of thiourea solution are added to one cc. of the solution. The formation of a bright yellow color indicates the presence of Bi. This is presumed to be a bismuth-thiourea comples(2).

To confirm the presence of bismuth, four drops of 1-methylbenzothiazole and three drops of Kl are added to one cc. of the solution. The formation of a brilliant red precipitate, of composition $C_8H_7NS \cdot KBiI_4$, proves the presence of Bi (3).

(3) In order to test for Mercury, one-half cc. of the test solution is poured on a filter paper, followed by one-half cc. of stannous chloride solution. Aniline is then dropped on the paper until black particles become visible. Mercurous chloride is reduced to free black mercury in the alkaline environment furnished by the aniline (4).

(4) In order to prove the presence of Manganese, one cc. of the solution is made basic with excess ammonia, and three drops of Benzidrine are added. The appearance of a bright blue color confirms the presence of Manganese. The exact composition of the precipitate is not known, but Feigl believes it to be an oxidization product of the organic compound(4).

(5) To test for Magnesium, one cc. of 10% NH_4NO_3 solution is added to one cc. of the test solution, and the metals then precipitated by ammonium hydroxide. Magnesium is not precipitated under these conditions and is detected in the filtrate by the addition of four drops of oxine

solution (5).

As a check, the filtrate is made basic with NaOH solution and two drops of Quinalizarine added to the hydroxide. The formation of a " cornflower blue " absorption lake proves the presence of Mg (6).

Section 6. IDENTIFICATION OF THE AMPHOTERIC GROUP.

The filtrate from the NaOH separation is made acid with 3N HCl solution and two cc. in excess are added. The solution is divided into four portions.

(1) The first portion of the test solution is heated to boiling in the presence of an iron nail and about one-half cc. is poured onto a piece of filter paper which has been soaked in cacothelein solution. The appearance of a violet color shows the presence of tin. The formula for this colored compound is not known, but it is also believed to be an oxidization product (7).

To confirm the presence of tin, another one-half cc. of test solution is poured on a piece of filter paper and the test described for mercury in group 11-B is repeated.

(2) Another half-cc. of the test solution is placed on a spot plate, a small crystal of potassium nitrate is placed in the solution, and a few drops of HCl are added. Two drops of Rhodamine B are added and the change of the color of the dye to violet with the formation of finely divided particles, proves the presence of Antimony.

The presence of antimony is further con-

CHART V.

ANALYSIS OF GROUP 11-A

Make the solution containing SbO_4^{---}, SnO_3^{--}, AlO_2^-, and CrO_2^- acid with 3N HCl. Divide into four equal parts.	
1.	To one two-cc. portion of the solution is added an iron nail and the mixture heated to boiling. This is divided into two parts. A portion is poured on a filter paper, followed by a solution of $HgCl_2$, and four drops of aniline. The appearance of black specks, proves the presence of Sn^{++++}. The other reduced portion is placed on a filter paper which has been saturated with cacotheline solution. The immediate formation of a violet color proves the presence of Sn^{++++}.
2.	A half cc. portion is placed on a spot plate and made strongly acid with 3N HCl. A small crystal of KNO_2 is placed in the solution and the mixture is agitated until the brown fumes cease to come off. Two drops of Rhodamine B are added. A violet, coagulated precipitate proves the presence of Sb^{+5}. To a one-cc. portion, three drops of acridine solution are added, followed by three drops of KI solution. The formation of a very heavy canary yellow precipitate shows the presence of Sb^{+++}.
3.	A one cc. portion is acidified with acetic acid, three drops of Aluminon are added, and the mixture is heated. The solution is made basic with ammonia. A reddish precipitate proves the presence of Al^{+++}.
4.	A two-cc. portion is made basic with ammonia and small portions of Na_2O_2 are added. The appearance of a yellow solution is indicative of the presence of Cr^{+++}. The solution is partially neutralized with conc. HCl and four drops of benzidine solution are added. The immediate formation of a blue precipitate proves the presence of Cr^{+++}.

firmed by the addition of 1-methylbenzothiazole to one cc. of solution. If antimony is present, a canary yellow solution and precipitate are formed (3).

(3) One cc. of test solution is made basic with ammonia solution, 0.5 gram of sodium peroxide is added, and the solution is warmed. A yellow color indicates the presence of chromium. On neutralizing the excess base with concentrated HCl, and adding benzidine, a blue solution is obtained (4).

(4) Another portion of test solution is made acid with acetic acid and one cc. in excess is added. Aluminon reagent is then added and the solution made basic with 3N ammonia. The formation of a bright red lake proves the presence of aluminum (8).

Section 7. IDENTIFICATION OF AMMONIA COMPLEX GROUP

This filtrate from the ammonium carbonate precipitation is divided into four parts.

(1) Six drops of dimethylglyoxime solution are added to one portion of the filtrate and the immediate appearance of a brilliant red precipitate proves the presence of Nickel. This organic compound has proved to be the most reliable reagent for nickel. No other has ever been found which equals it in sensitivity.

(2) Another portion of the solution is acidified with 3N HCl. One cc. of this is treated with six drops of a-nitroso-b-naphthol which, in the presence of cobalt, forms a purple-red precipitate. This reagent will detect one part

of cobalt in 1,000,000 of solution.

(3) A third portion of the filtrate is acidified with acetic acid, salicyaldoxime (three drops) is added to one cc. of this solution and, in the presence of copper, a heavy greenish precipitate is formed(9).

As further confirmation, of the presence of copper, four drops of cupferron solution are added to one cc. of the acid solution. The formation of a heavy greenish precipitate proves the presence of copper (10).

(4) Another portion of the test solution is acidified with 3N HCl. Three normal NaOH solution is then added to precipitate the insoluble hydroxides of Cu'',Cd'',Co'', and Ni'' and to dissolve the Zn'' hydroxide. This filtrate is acidified with acetic acid and to one cc., six drops of oxine solution are added. The formation of a heavy yellow precipitate proves the presence of Zn (11).

(5) The residue from the NaOH separation above is dissolved in 3N acetic acid and one cc. in excess added. Oxine solution is added until the precipitation is complete. The solid is filtered off and the filtrate is made basic with ammonia. The appearance of a heavy yellow precipitate shows the presence of Cadmium (11).

CHART V11.

ANALYSIS OF GROUP 111-A

	The filtrate from the ammonium hydroxide treatment is divided into four equal portions.
1.	A one-cc. portion is treated with dimethylglyoxime. A heavy red precipitate proves the presence of Ni''.
2.	A one-cc. portion is made acid with 3N HCl and one cc. in excess is added. Four drops of a-nitroso-b-naphthol are added, and the formation of a heavy purple-red precipitate proves the presence of Co''.
3.	A one-cc. portion is acidified with 3M HOAc and one cc. is added in excess. Three drops of salicaldoxime reagent are added. The formation of a greenish precipitate proves the presence of Cu''. Another one-cc. portion is acidified with 3N HCl and one cc. is added in excess. Four drops of cupferron solution are added and the formation of a bluish precipitate proves the presence of Cu''.
4a.	A two-cc. portion is acidified with HOAc and then made basic with NaOH, one cc. being added in excess. The mixture is filtered and the residue saved for treatment according to 4b., below. The filtrate is treated with four drops of oxine solution. The formation of a heavy yellow precipitate proves the presence of Zn''.
4b.	The residue from the above treatment is dissolved in 3M HOAc solution and one cc. in excess is added, and the mixture is filtered. The filtrate is made basic with ammonia and two drops of oxine are again added. A heavy yellow precipitate proves the presence of Cd''.

Section 8. IDENTIFICATION OF THE CARBONATE GROUP.

The residue, consisting of the carbonates of barium, calcium, and strontium, is dissolved in 6N HOAc and the solution is made neutral with 3N ammonia.

(1) About one cc. of this neutral solution is poured onto a piece of filter paper, and two drops of Sodium Rhodizonate solution are added. The appearance of a red speck indicates the presence of either Ba or Sr. If the color disappears upon the addition of 3N HCl solution, only Sr is present. If the color remains, both Ba and Sr may be present.

In order to distinguish between these two elements, they are converted into the insoluble chromates, in which form barium does not react with the reagent, while strontium does. One cc. of the test solution is poured onto a piece of filter paper which has been saturated with potassium chromate solution. Again two drops of sodium rhodizonate are added to the paper. The appearance of a red speck proves the presence of strontium (4).

(2) One cc. of the neutral test solution is treated with one cc. of NH_4NO_3 solution, and one-half cc. of $K_4Fe(CN)_6$ is then added. A white crystalline precipitate proves the presence of Ca(12).

CHART Vl.

ANALYSIS of GROUP lll-B

Dissolve the precipitate, consisting of the carbonates of Ba'',Sr'', and Ca'' in 6N HOAc. Then make neutral with ammonium hydroxide. Divide into three portions.	
1.	A half-cc. portion is poured on filter paper and treated with two drops of sodium rhodizonate solution. A red precipitate shows the presence of either barium or strontium. A few drops of 3N HCl are added to the paper and if the precipitate dissolves, only Sr'' is present. If it does not dissolve, either Ba'' or Sr'', may be present, or both. An one-cc. portion is poured on filter paper which has been saturated with potassium chromate. Sodium rhodizonate solution is now added. A red precipitate proves the presence of Sr''.
2.	One cc. of a 50% solution of NH_4Cl is added to a one-cc. portion of the solution. Five drops of $K_4Fe(CN)_6$ solution are added. The formation of a white crystalline precipitate proves the presence of Ca.

Section 9. IDENTIFICATION OF THE ALKALINE GROUP.

The filtrate from the ammonium carbonic separation is evaporated almost to dryness. Five cc. of concentrated nitric acid are added to the solution and evaporation is completed to dryness. The residue is heated until all the ammonium salts are completely volatilized. A portion of the residue is placed in the flame on a platinum wire. The immediate appearance of an intensely whitish-yellow flame, persisting for at least five seconds, shows the presence of sodium. A violet flame indicates the presence of potassium. If sodium is found to be present, the test should be repeated and the flame viewed through several thicknesses of cobalt glass. Under these conditions, the yellow color of sodium is completely masked, and the red-violet color of the potassium flame will be visible (8).

The remainder of the salts is dissolved in 5 cc. of water, with heating if necessary. Two cc. of a hot 2% olution of Naphthol Yellow S are added to this and the mixture is allowed to stand at room temperature for several minutes. The formation of a flocculent yellow precipitate proves the presence of potassium (13).

The test for ammonia is made on a portion of the original solution. Five cc. of the original solution are placed in a beaker and 6N NaOH is added with stirring until the solution is strongly alkaline. A piece of moistened red litmus paper is placed on the convex side of a watch glass,

which then is placed over the beaker. The solution is warmed gently without boiling. An immediate, uniform change of color in the litmus from red to blue, without the formation of deep blue spots, indicates the presence of ammonia.

CHART V111

ANALYSIS OF GROUP 1V

Evaporate the filtrate from Group 111 separation almost to dryness, and then add 10 cc. of concentrated nitric acid. Now evaporate completely to dryness and heat until all the ammonium salts are destroyed.

Portions of the residue are tested in the flame for Na' and K'.

A violet coloration around the particle on the platinum wire shows the presence of K'.

A brilliant yellow flame persisting for 10 seconds shows the presence of Na'.

If Na' is shown to be present, the test for Potassium is repeated and the flam viewed through several thicknesses of cobalt glass.

The residue is dissolved in 5 cc. of water, warming if necessary. Two cc. of a hot 2% solution of Naphthol Yellow S are added and the mixture is allowed to stand at room temperature. A flocculent yellow precipitate indicates the presence of potassium

SCHEME 11

PHOSPHATES AND ARSENATES PRESENT

As stated above, the presence of arsenate or phosphate in the original solution will cause an interference in the subsequent analysis for the metallic ions. If either or both of these acids has been shown to be present, a slight modification of the procedure outlined in Scheme 1 will be necessary.

The solution is prepared and the precipitation and analysis of the Silver Group is carried out exactly as described in Sections 1 and 2 above.

Upon the addition of ammonium hydroxide to the filtrate after the removal of the Silver Group, the insoluble hydroxides of Bi^{+++}, Mn^{+++}, Fe^{+++}, Mg^{++}, Cr^{+++},Al^{+++}, and Sn^{++++} and $HgNH_2Cl$, Sb_2O_3 and the phosphates of Ba^{++}, Ca^{++}, and Sr^{++} will precipitate. Twenty cc. of 6N NaOH are added to dissolve the amphoteric hydroxides as Group 11-A.

The residue, consisting of the insoluble hydroxides of Bi^{+++},Mn^{++}, Fe^{++}, and Mg^{++} and $HgNH_2Cl$, and the phosphates of Ba^{++},Ca^{++}, and Sr^{++} is dissolved in HCl, with heating, if necessary. Five cc. of ammonia sulfate solution are added in order to precipitate the insoluble sulfates of Ba,Sr, and Ca. This is filtered and the filtrate is designated as Group 11-B.

The residue from the ammonium sulfate treatment, consisting of the insoluble sulfates of Ba, Sr, and Ca, is placed in a beaker and five cc. of sodium carbonate solution are added. The mixture is boiled for ten minutes, and then filtered. The residue consists of the carbonates of Ba'', Sr'', and Ca'', and is designated as Group lll. The ions of this group are identified according to the method described in Scheme 1.

The phosphate and arsenate ions are found in Group ll-B and will not interfere with any test except that of magnesium. In order to prevent the interference of insoluble ferric hydroxide or phosphate with the test for magnesium, one cc. of sodium tartrate solution is added to one cc. of the solution to be tested. This forms a ferric-tartrate complex from which the iron is not precipitated even in strongly basic solution. Ammonium hydroxide is now added to the solution, followed by the addition of four drops of diphenylcarbazide solution. The formation of a purple colored supernatent liquid proves the presence of Magnesium (8).

The remaining groups are unchanged and are separated and identified exactly as described in the procedure of Scheme 1.

V. REAGENTS

Acridine: 1.0 gram in 100 cc. of EtOH

Aluminon: 0.1% aqueous solution

Aminopyrine: 1.0 gram in 100 cc. of water

Aniline: C.P. undiluted

Benzidine: 0.05 gram dissolved in 10 cc. of acetic acid, diluted to 100 cc. with water and filtered.

Cacotheline: Saturated aqueous solution

Cupferron: 2.0 gram in 100 cc. of water

Dimethylglyoxime: 1.0 gram in 100 cc. of EtOH

Hydroquinone Reagent: Mix solutions A,B, and C in the ratio 2:1:1 by volume.

Solution A: Five grams of ammonium molybdate are dissolved in 60 cc. of water and 40 cc. of water are added containing 15 cc. of conc. sulfuric acid.

Solution B: Twenty grams of sodium sulfite are dissolved in 100 cc. of water.

Solution C: Five-tenths gram of hydroquinone are dissolved in 100 cc. of water and 1 cc. of N sulfuric acid are added.

Oxine (8-hydroxyquinoline: Four grams are dissolved in 10 cc. of HOAc and diluted to 100 cc. with water.

1-methylbenzothiazole: One cc. in 50 cc. of EtOH.

Naphthol Yellow S: 1.5 grams in 100 cc. of water.

a-nitroso-b-naphthol:	One gram in 50 cc. of HOAc and dilute to 100 cc. with water.
Potassium thiocyanate:	One percent aqueous solution
Quinalizarin:	One mg. in 100 cc. of EtOH
Rhodamine B:	Ten mg. in 100 cc. of water
Salicyaldoxime:	One gram of reagent dissolved in 5 cc. of EtOH and poured slowly into 95 cc. of water. This is filtered when it becomes clear.
Sodium Rhodizonate:	One-tenth percent aqueous solution
Thiourea:	Five percent aqueous solution.

VI. BIBLIOGRAPHY

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